

KOKAI PATENT APPLICATION NO. SHO 57-159645

**CONDUCTIVE LAMINATE**

[Translated from Japanese]

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## CONDUCTIVE LAMINATE

*[Dohdensei sekisohtai]*

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*[There are no amendments to this patent.]*

*[Translator's note: Many numbers were barely legible in the source document. Best guesses have been made.]*

*[Translator's note: Names of products and companies are spelled phonetically in this translation.]*

### Specification

#### 1. Title of invention

Conductive laminate

#### 2. Claim of the invention

A conductive laminate in which a silicon compound layer (B) mainly comprising an organic silicon compound, a transparent conductive layer (C) comprising a metal oxide, and silicon compound layer (D) mainly comprising an organic silicon compound are successively laminated onto the surface of an organic polymer molding (A).

#### 3. Detailed description of the invention

The present invention pertains to a conductive laminate and the invention further pertains to an organic polymer molding provided with a tough transparent conductive layer.

Conductive laminates having a transparent conductive film on the surface of an organic polymer molding (a film, in many cases) has many advantages such as high transparency,

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flexibility, and processability; however, in comparison to conductive glasses, adhesion between the transparent conductive layer and organic polymer molding, mechanical properties such as abrasion resistance, etc. are inferior. As a means to eliminate the aforementioned problems, a method in which a thin film of inorganic silicon or silicon compound (oxide, nitride, etc.) is provided on a polymer film ahead of time and a transparent conductive film is subsequently formed (see Japanese Kokai [Unexamined] Patent Application No. Sho 52-67647 for reference) has been proposed.

When a silicon thin film is provided, the surface of the polymer film becomes similar to that of the glass substrate and an increase in adhesive strength between the transparent conductive film and polymer film can be achieved, but the degree of improvement is a mere 2 to 3 times at most. When the substrate is glass, a method where a silicon dioxide film is provided on an indium oxide type film at a substrate temperature in the range of 350°C to 500°C to prevent a change in indium oxide type transparent conductive film has been proposed (see Japanese Kokoku [Examined] Patent Application No. Sho 49-18446 and Japanese Kokai [Unexamined] Patent Application No. Sho 53-81144 for reference). An improvement in the mechanical properties is expected in the aforementioned method, but a high substrate temperature is required for the aforementioned method and the method cannot be used for a conductive laminates comprising substrates having low heat-resistance such as organic polymer moldings.

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Also, in the case of a flexible substrate, a method where a silicon oxide protective layer is provided for a transparent conductive layer comprising a metal oxide for an increase in abrasion resistance has been proposed (see Japanese Kokai [Unexamined] Patent Application No. Sho 53-67408 for reference). In the aforementioned method, heating of the substrate is not especially provided and a silicon oxide layer is formed, and the silicon oxide layer is hard but is brittle and cracking or peeling of the film occurs and production of a conductive laminate having flexibility and abrasion resistance is not possible.

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As a result of much research conducted by the present inventors on superior conductive organic polymer moldings having high adhesion as well as abrasion resistance, the inventors discovered that the target performance could be achieved when a thin film having a sandwich structure where transparent conductive layer (C) is sandwiched between silicon compound layers (B) and (D) is laminated onto the surface of organic polymer molding (A), and as a result, the present invention was accomplished.

Thus, the present invention is a conductive laminate in which a silicon compound layer (B) mainly comprising an organic silicon compound, a transparent conductive layer (C) comprising a metal oxide, and a silicon compound layer (D) mainly comprising an organic silicon compound are successively laminated onto the surface of organic polymer molding (A).

The present invention is a conductive laminate that fully utilizes the features of organic silicon compounds. The organic silicon compound has a high affinity with both of the inorganic phase and the organic phase and increases adhesion between the organic polymer molding (A) and the transparent conductive layer (C). Furthermore, when the aforementioned transparent conductive layer (C) is covered with an organic silicon compound, a significant increase in abrasion resistance can be achieved without sacrificing flexibility of the conductive laminate.

The organic polymer compound comprising the organic polymer molding (A) in the present invention is not especially limited as long as it is an organic polymer compound having high heat-resistance, and in general, a heat-resistance of 80°C or higher, preferably, 100°C or higher, and especially, 120°C or higher, for example, polyimide, polyether sulfone, polysulfone, polyhydantoin, polyethylene terephthalate, polyethylene-2,6-naphthalene dicarboxylate, polydiallyl phosphate, polycarbonate and other polyester type resins, and furthermore, aromatic polyamide, polyamide, polypropylene, cellulose triacetate, etc. can be mentioned. Among those listed above, polyethylene terephthalate which has high transparency, flexibility, and desirable mechanical properties is especially suitable. Needless to say, the aforementioned compounds can be used as homopolymers, copolymers, or blend polymers.

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The shape of the aforementioned organic polymer molding is not especially limited, but, in general, either a sheet or film is desirable, and films, in particular, are especially desirable since winding is possible and continuous production can be achieved. When used as a film, the thickness of the film is preferably in the range of 6-500  $\mu$ , and especially, in the range of 12-125  $\mu$ .

Furthermore, when the aforementioned film is transparent, the laminated of the present invention is transparent as well, but pigments may be added or a surface treatment, for example, sand matting treatment, etc., may be provided as well. When a sand matting treatment is provided, the effect of the present invention can be further enhanced.

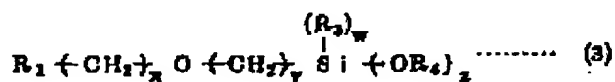
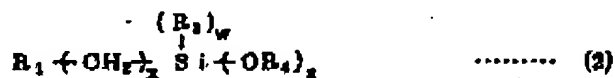
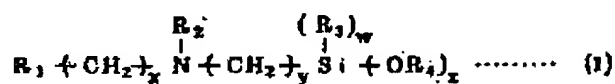
Furthermore, organic silicon compound that comprises layer (B) is an organic metal compound having a group having affinity for or that forms a chemical bond with the inorganic phase and a group having affinity for or that forms a chemical bond with the organic phase at the same time, and is an organic compound containing silicon (Si).

For the aforementioned group having affinity with or forming a chemical bond with the inorganic phase, groups that can be converted to a hydroxyl group as a result of an hydrolysis reaction, for example, alkoxy groups, in particular, alkoxy groups with 4 or fewer carbon atoms, halogen atoms, tert-butyl peroxy groups and acyl groups can be mentioned, and for the aforementioned group having affinity with or forming a chemical bond with the organic phase, a lower alkyl group, phenyl group, (meth)acryloxy group, (meth)acryloxy propyl group, vinyl group, epoxy group, or a substituted or non-substituted amino group can be mentioned.

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For the aforementioned compounds, compounds shown in the general formulas shown below:

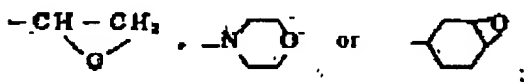
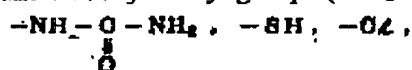
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[where, in the formula, R<sub>1</sub> is a group shown in the formulas below



[where, in the formula, R<sub>5</sub> and R<sub>6</sub> are each, independently, a group selected from hydrogen, alkyl groups with 1-4 carbon atoms, hydroxy alkyl groups, phenyl groups, allyl groups (-CH<sub>2</sub>-CH=CH<sub>2</sub>) and carboxy methyl groups (-CH<sub>2</sub>-COOH).],



R<sub>2</sub> is either a hydrogen or an alkyl group with 1-12 carbon atoms; R<sub>3</sub> and R<sub>4</sub> are each, independently, an alkyl group with 1-4 carbon atoms; x and y is an integer in the range of 1-12; w is either 0 or an integer of 1-2; xz is an integer of 1-3, and w+z=3.]

and the compounds shown in general formula (4)



[provided that in the formula, R is an organic group such as methyl, ethyl, propyl, butyl, vinyl, phenyl, methacryloxy and methacryloxy propyl; X is a halogen, alkoxy group, tertiary butyl peroxy group, or acryl group; m is an integer in the range of 1 to 3 and satisfies n+m=4.]

and prepolymers produced by hydrolysis of the aforementioned compounds can be used effectively. The aforementioned organic silicon compounds may be used as a mixture with other

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organic metal compounds, for example, organic titanium compounds, and furthermore, an appropriate amount of curing catalysts, adhesive enhancers, wetting agents, plasticizers, a variety of stabilizers, flame retardants, antioxidants, lubricants, foaming agents, and/or thickeners may be mixed as needed.

The aforementioned compounds may be used as is or after dissolving in a solvent. For examples of the aforementioned solvents, one or mixtures of methanol, ethanol, isopropanol, n-butanol, toluene and ethyl acetate can be mentioned.

The thickness of the layer (B) mainly comprising the aforementioned organic silicon compound is not especially limited and a thickness in the range of 0.01-1  $\mu$  is desirable. From the standpoint of abrasion resistance and optical properties, a thickness in the range of 0.05-0.5  $\mu$  is further desirable. When the thickness is 0.01  $\mu$ , formation of continuous film is less likely to be achieved, and the initial purpose cannot be achieved. On the other hand, when the thickness exceeds 1  $\mu$ , formation of cracks or loss of plasticity of the organic polymer moldings occurs.

Upon coating the aforementioned organic silicon compound, known coaters and coating methods such as doctor knife, bar coater, gravure roll coater, curtain coater, and knife coater, spray coating, dip coating, etc. may be used according to the shape and properties of the organic polymer molding and organic silicon compound.

The aforementioned organic silicon compound is coated onto an organic polymer molding and dried, then, cured by heating, ionic bombardment, or radiation such as ultraviolet rays,  $\beta$ -rays, or  $\gamma$ -ray.

For the metal oxide used in the present invention, one or more metal oxides selected among the group consisting of indium, tin, cadmium, zirconium, and titanium can be mentioned. The aforementioned metal oxides initially are transparent electric insulating materials, but become semiconductors when (1) a trace amount of impurities is included, (2) a slight oxygen deficiency exists, (3) oxides of two or more metals are used, etc. It is necessary for the metal oxide that comprises the transparent conductive film of the present invention to be a semiconductor. As



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suitable semiconductor metal oxides, for example, tin doped indium oxide  $[(\text{In})_{2-x}(\text{Sn})_x\text{O}_{3-x}]$ , antimony doped tin oxide  $[(\text{Sn})_{2-m}(\text{Sb})_m\text{O}_{2-n}]$ , cadmium tin oxide ( $\text{Cd}_2\text{SnO}_4$ ), etc. can be mentioned..

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In order to achieve sufficient conductivity, it is desirable when the film thickness of the aforementioned oxide film is at least 10 Å and at least 30 Å is preferable. Furthermore, in order to produce a film having a sufficient transparency, a film thickness of not more than 5000 Å is desirable, and not more than 3000 Å is preferable. As a method used for providing the aforementioned semiconductor metal oxide film onto layer (B) mainly comprising an organic silicon compound, (1) sputtering process, (2) vacuum deposition process, (3) ion plating process, etc. can be mentioned.

For the sputtering process, standard methods may be used and in this case, low-temperature sputtering where the plasma is confined to the region around the target and the molding substrate is arranged outside the plasma can be used effectively. For vacuum deposition, a variety of standard methods may be used. For example, resistance heating method, high-frequency induction heating method, electron beam heating method, etc. can be mentioned. Furthermore, a reactive deposition method where deposition is provided for a metal under an oxygen gas atmosphere can be mentioned.

For ion plating, a variety of standard methods may be used, and discharge in a high-frequency electric field at 1356 MHz and high-frequency ion plating under a DC electric field can be used effectively.

Upon formation of transparent conductive layer (C) based on the aforementioned methods, when the oxygen partial pressure is low or formation rate is high, the film produced becomes a lower grade oxide film and transparency and conductivity are slightly lower but when high transparency and conductivity are not required, it is sufficient. However, when high transparency and conductivity are required, a heat-treatment (annealing) is provided after the aforementioned

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film formation.

When a heat-treatment is provided under an oxygen atmosphere such as in air, oxidation, and crystallization of the metal oxide film are promoted and an increase in transparency and conductivity of the film results.

The organic silicon compound comprising layer (D) of the present invention comprises one or more compounds selected from among the organic silicon compounds comprising layer (B) of the present invention, and the same organic silicon compound that comprises layer (B) or a different compound may be used or a part may be the same as layer (B).

The aforementioned organic silicon compound can be used as a mixture with other organic metal compounds, for example, an organic titanium compound, and furthermore, appropriate amounts of curing catalysts, adhesive enhancers, wetting agents, plasticizers, a variety of stabilizers, flame retardants, antioxidants, lubricants, foaming agents and/or thickeners may be included as needed.

The aforementioned compound may be used as is or after dissolving in a solvent. For examples of the aforementioned solvents, one or a combination of methanol, ethanol, isopropanol, n-butanol, toluene and ethyl acetate can be mentioned. The thickness of layer (D) mainly comprising the aforementioned organic silicon compound is not especially limited but a thickness in the range of 0.01-1  $\mu$  is suitable. From the standpoint of abrasion resistance and optical properties, a thickness in the range of 0.05-0.5  $\mu$  is especially desirable. When the thickness is less than 0.01  $\mu$ , formation of a continuous film is less likely to be achieved, and the initial purpose cannot be achieved. On the other hand, when the thickness exceeds 1  $\mu$ , formation of cracks, loss of conductivity on the surface, or loss of plasticity of the organic polymer molding occurs.

Upon coating the aforementioned organic silicon compound, known coaters and coating methods such as doctor knife, bar coater, gravure roll coater, curtain coater, and knife coater, spray coating, dip coating, etc. may be used according to the shape and properties of the organic polymer moldings and organic silicon compound.

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The aforementioned organic silicon compound is coated onto the organic polymer molding and dried, then, cured by heating, ionic bombardment, or application of radiation such as ultraviolet rays,  $\beta$ -rays, or  $\gamma$ -rays.

In comparison to conductive laminates produced by conventional methods, the aforementioned conductive laminate of the present invention has the higher mechanical properties such as adhesivity and abrasion resistance of the transparent conductive layer, and can be used effectively for a wide range of materials for purposes such as electrophotography, antistatic materials, surface heating units, solid displays, optical memory, photoelectric conversion elements, optical communication devices, optical information processing, and solar energy materials.

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It is especially suitable as a leader tape where abrasion resistance is required. A leader tape without an antistatic treatment is likely to take on a static electric charge and dust and dirt are picked up by the static electricity and eventually are adsorbed on the magnetic surface of magnetic head and become a cause of dropout, output reduction, etc., but when the conductive laminate of the present invention is used, static electricity can be prevented without being influenced by humidity. And furthermore, abrasion resistance is high, thus, the antistatic property cannot be easily lost as a result of contact with the magnetic head. Furthermore, clogging of the head as a result of scraping of the surface of the leader tape does not occur.

The present invention is explained further in specific terms with working examples below.  
Working Example 1 and Comparative Examples 1-7

An alcohol solution of methanol, ethanol, and isopropanol containing 0.7 wt% of "NUC Silicon Primer" (product of Japan Unika Co., Ltd.) was coated onto a polyethylene terephthalate film with a thickness of 25  $\mu$  by gravure coater and dried for 1 minute at a temperature of 150°C. The film thickness of the organic silicon compound after drying was 700 Å. The film produced is hereinafter referred to as film (a). For comparison, SiO<sub>2</sub> was deposited onto a polyethylene terephthalate film with a thickness of 25  $\mu$  under  $7 \times 10^{-5}$  Torr. The film thickness of the inorganic

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silicon compound layer was 1000 Å. The aforementioned film produced is hereinafter referred to as film (b). A mixture comprising 95 wt% of  $\text{In}_2\text{O}_3$  and 5 wt% of  $\text{SnO}_2$  was deposited onto each of the aforementioned film (a), film (b), and a non-treated polyethylene terephthalate with a thickness of 25  $\mu$  under  $8 \times 10^{-5}$  Torr. The thickness of the metal oxide layer was 100 Å. Furthermore, a heat treatment was provided at a temperature of 150°C to produce a transparent conductive film. An organic silicon compound layer or an inorganic silicon compound layer was laminated onto the transparent conductive layer of each of the transparent conductive films to produce conductive laminates.

Each of the aforementioned 7 samples was slit to a width of 1/2 inch to form leader tapes for video cassettes. Furthermore, transmittance, surface resistance, and abrasion resistance of the aforementioned leader tapes were evaluated and the results obtained are shown in Table I below.

It should be noted that the abrasion resistance (still time) means the time until the film is scraped and scratches are formed in the substrate when the rotating magnetic head is run at the same position of the tape while the tape is in a stationary state.

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Table I

	Appl. Ex. 1	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
Layer B	NUC silicone 700 Å	NUC silicone 700 Å	NUC silicone 700 Å	SiO <sub>x</sub> 1000 Å	SiO <sub>x</sub> 1000 Å	SiO <sub>x</sub> 1000 Å	---	---
Layer D	NUC silicone 800 Å	SiO <sub>x</sub> 1000 Å	---	NUC silicone 800 Å	SiO <sub>x</sub> 1000 Å	---	NUC silicone 800 Å	SiO <sub>x</sub> 1000 Å
Transmittance (%)	88	88	87	88	88	87	87	87
Surface resistance (KΩ/square)	12	15	9	20	25	15	28	30
abrasion resistance (still time)	10 min	50 sec	12 sec	40 sec	30 sec	10 sec	20 sec	15 sec

## Working Examples 2 and 3 and Comparative Examples 8-10

An organic silicon compound layer was formed on a polyethylene terephthalate film with a thickness of 25  $\mu$  as in the case of the aforementioned Working Example 1. The thickness of the organic silicon compound layer was 800 Å.

A mixture comprising 95 wt% of In<sub>2</sub>O<sub>3</sub> and 5 wt% of SnO<sub>2</sub> was deposited onto each of the aforementioned films under 8x10<sup>-5</sup> Torr. The thickness of the metal oxide layer was 100 Å.

And furthermore, an organic silicon compound layer was formed on the aforementioned metal oxide layer as in the case of Working Example 1.

The aforementioned samples were slit to a width of 1/2 inch to form leader tapes. Furthermore, transmittance, surface resistance, and abrasion resistance (still time) of the aforementioned leader tapes were evaluated and the results obtained are shown in Table I below.

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Table II

	Comp. Ex. 8	Appl. Ex. 2	Appl. Ex. 3	Comp. Ex. 9	Comp. Ex. 10
Layer B	NUC Silicone 800 Å	NUC Silicone 800 Å	NUC Silicone 800 Å	NUC Silicone 800 Å	NUC Silicone 800 Å
Layer D	NUC Silicone 90 Å	NUC Silicone 700 Å	NUC Silicone 3000 Å	NUC Silicone 6000 Å	NUC Silicone 12000 Å
Transmittance (%)	62	63	63	63	63
Surface resistance ( $\Omega$ /square)	$3 \times 10^5$	$5 \times 10^5$	$6 \times 10^5$	$1 \times 10^6$	$> 10^{10}$
abrasion resistance (still time)	30 sec	19 min	8 min	1 min	---

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## Working Example 4

A coating solution prepared by dissolving 10 wt% of  $\gamma$ -methacryloxy propyl trimethoxy silane (product of Shinetsu Chemical Co., Ltd., trade name KBM503) in a mixed solvent of 90 wt% ethanol and 10 wt% water was coated onto a polyethylene terephthalate film with a thickness of 25  $\mu$  by gravure roll coater and dried for 1 minute at a temperature of 150°C. The thickness of the film of the organic silicon compound after drying was 800 Å.

Furthermore, an alloy target of 90 wt% In and 10 wt% of Sn was used and sputtering was done for the organic silicon compound layer under an argon-oxygen gas mixture (oxygen content 20 vol%) at  $5 \times 10^{-3}$  Torr and a transparent conductive layer (film thickness 100 Å) was produced by DC sputtering.

Subsequently, an organic silicon compound layer (film thickness 1000 Å) was formed on the transparent conductive layer in the same manner.

The aforementioned samples were slit to a width of 1/2 inch to form leader tapes. The surface resistance of the leader tape produced was 16 K $\Omega$ /square and transmittance was 86%.

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When an the abrasion resistance was examined as in Working Example 1 above, the still time was 9 minutes.

## Working Example 5

The aforementioned organic silicon compound was changed to vinyl tris( $\beta$ -methoxyethoxy) silane (product of Shinetsu Chemical Co., Ltd., trade name KBC1003) and a leader tape with a width of 1/2 inch was produced as in Working Example 2 above. The surface resistance of the leader tape produced was 18 K $\Omega$ /square and transmittance was 86%.

When an examination the abrasion resistance was examined as in Working Example 1, the still time was 9 minutes.

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